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POLYSILANE-POLY(FERROCENYLSILANE) RANDOM COPOLYMERS.

by

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Polysilane - Poly(ferrocenylsilane) Random Copolymers

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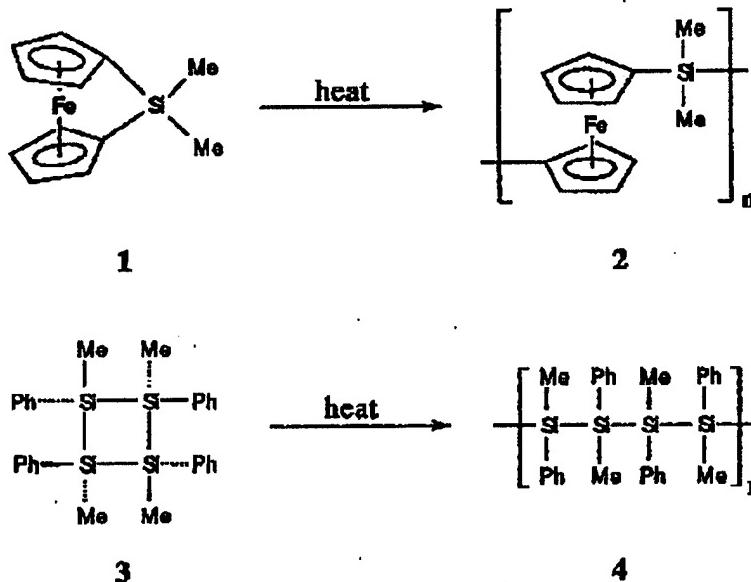
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Polymers based on inorganic elements continue to attract considerable interest because of their unique physical and chemical properties.¹ Polysilanes $[SiR_2]_n$ represent a novel class of these materials which exhibit σ -delocalization, photosensitivity, and thermochromic behaviour.^{1,2} Such characteristics have led to potential applications as photoconductors and photoresists. In addition, these polymers have also attracted attention as ceramic precursors.² Polysilanes have been prepared via a variety of methods including Wurtz² and dehydrogenative³ coupling, anionic polymerization of masked disilenes,⁴ and recently by ring-opening polymerization (ROP).^{5,6} In 1992 the synthesis of high molecular weight poly(ferrocenylsilanes) via the thermal ROP of silicon-bridged [1]ferrocenophanes was described.⁷ These macromolecules possess a main chain of alternating ferrocene and organosilane units and exhibit a range of interesting properties as a result of the presence of transition metals in the polymer backbone.⁸ The synthesis of copolymers of polysilanes and poly(ferrocenylsilanes) offers the possibility of tuning physical characteristics and of providing access to materials with unusual combinations of properties.⁹ In this communication we report on our attempts to thermally copolymerize cyclic silanes and silicon-bridged [1]ferrocenophanes.

The [1]ferrocenophane **1** polymerizes thermally at elevated temperatures in the melt to yield the poly(ferrocenylsilane) **2**. In addition, the anionic ROP of **3** in solution has been previously reported.⁵

We have now found that 3 also polymerizes thermally at 150°C to quantitatively yield poly(methylphenylsilane) 4. Indeed, when the ROP of 3 was monitored by Differential Scanning Calorimetry (DSC), a large broad exotherm at 150°C was detected with an onset temperature of 90°C. Integration revealed the strain energy to be ca. 56 kJmol⁻¹, which is less than that determined for 1 (ca. 80 kJmol⁻¹) by similar methods.⁷

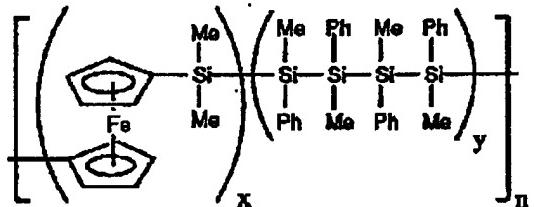


Thermal copolymerization experiments involving mixtures of 1 and 3 were carried out in various ratios (Table 1) and were performed in sealed, evacuated Pyrex tubes at 150 °C for 2 h. Under these conditions the reaction mixture transformed from a red melt into an immobile amber colored glass. Analysis of 5a - 5c by ¹H NMR (in C₆D₆) confirmed that no unreacted monomer 1 or 3 remained. The polymeric products 5a - 5c were isolated as pale amber powders by precipitation from THF into hexanes and possessed number average molecular weights (M_n) of 67,000 - 89,000.

Evidence that 5a - 5c are true copolymers rather than blends of the two homopolymers was provided by the use of Gel Permeation Chromatography (GPC) with an on-line photo diode array detector, which allows for the simultaneous observation of multiple wavelengths. GPC traces for 5a -

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5c showed two absorptions at 330 nm and 450 nm which are close to those for poly(methylphenylsilane) and poly(ferrocenyldimethylsilane), respectively.^{2,10} The two traces overlaped exactly, which indicated that unless two homopolymers with identical molecular weights were present, the two different monomers were incorporated into a single copolymer. Photochemical degradation was found to be selective for the methylphenylsilane units, leaving the ferrocenylsilane segments intact. Thus, when photodegradation of 5 was carried out in THF using 340 nm UV light for 18 h, a GPC trace of the products showed no absorption at 330 nm indicating the absence of polysilane segments. In addition, the absorption at 450 nm for the ferrocenylsilane segments shifted to a shorter retention time (lower molecular weight) indicating that no high polymer remained. From the molecular weight of the degraded polymer it was possible to obtain the degree of polymerization of the ferrocenylsilane segments; in all cases this was relatively low (DP = 2 - 10) but an increase was detected as the amount of 1 in the initial monomer mixture was increased. The λ_{max} for the polysilane segments increased with an increasing proportion of 3 in the monomer mixture, ranging from 325 nm for 5a to 333 nm for 5c. These absorption values suggest that the polysilane segments are relatively short and do not approach the limit corresponding to $M_n = 3,000$ where the λ_{max} levels off at 338 nm.² This data indicated that 5a - 5c are copolymers which contain short segments of polysilane and poly(ferrocenylsilane).



5

Further structural characterization of 5a - 5c was provided by ^1H and ^{29}Si NMR spectroscopy. The ^1H NMR spectra of 5a - 5c (in C_6D_6) showed sharp signals for the ferrocenylidimethylsilane segments at 0.51 ppm (SiMe_2), and at 4.08 and 4.48 ppm ($\eta\text{-C}_5\text{H}_4$) and two broad signals for methylphenylsilane segments at -0.5 to 0.5 (Me) and 6.5 - 7.5 ppm (Ph).^{7,11} The integration ratio of the phenyl and cyclopentadienyl regions of the ^1H NMR spectra of 5 confirmed that the relative amounts of 2 and 4 in

the copolymers 5 were equal to the relative amounts of the two monomers 1 and 3 in the initial mixture prior to polymerization. Smaller, unresolved cyclopentadienyl resonances between 3.5 and 4.4 ppm were assigned to the ferrocenylsilane units near a juncture to a methylphenylsilane segment. Analysis of 5a - 5c by ^{29}Si NMR (in C₆D₆) showed resonances for ferrocenyldimethylsilane units at -6.4 ppm, a broad resonance for atactic methylphenylsilane segments from -37 to -40 ppm, and also revealed small peaks for SiMe₂ cross over groups between the ferrocenylsilane and methylphenylsilane segments at -6.6 and at -17.3 ppm.¹² The peaks are particularly apparent in the ^{29}Si NMR spectrum of polymer 5c which possessed relatively short ferrocenylsilane blocks; in contrast, the resonances in the corresponding spectrum of 5a are less intense as the ferrocenylsilane blocks are longer (Figure 1).

Cyclic voltammetric studies of 5a - 5d in CH₂Cl₂ showed the presence of two reversible oxidations at E_{1/2} = 0.00 V and at 0.23 V¹³ due to interacting iron atoms as found previously for poly(ferrocenylsilane) homopolymers.^{7,8} An irreversible oxidation with E_{p(ox)} = 0.39 V was also detected which corresponds to oxidation of the polysilane segments.¹⁴

In summary, the thermal ROP of mixtures of 1 and 3 provides a route to novel polysilane - poly(ferrocenylsilane) copolymers. It is interesting to note that these polymer structures are not available from the ROP of oligosilane-bridged [n]ferrocenophanes (n > 1) as such species are insufficiently strained to polymerize.⁸ The exact composition of the copolymers was found to depend on the initial ratio of monomers 1 and 3, but all are segmental in nature with alternating oligoferrocenylsilane and oligosilane blocks. Attempts to extend the scope of this type of copolymerization reaction are underway and we are also investigating the electronic and optical properties of the copolymers in detail.

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9. a) Low molecular weight polymers ($M_w = 3,500$) consisting of ferrocene and hexasilane units have been recently prepared by the polycondensation reaction of dilithioferrocene.tmeda with 1,6-dichlorohexasilane. Tanaka, M.; Truyuki, H. *Bull. Chem. Soc. Jpn.* 1993, 66, 334.
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12. We assign the ^{29}Si NMR resonances at - 17.3 and- 6.6 ppm to ...FcSiMe₂FcSiMe₂(SiMe₂)₄... and ...FcSiMe₂FcSiMe₂(SiMe₂)₄... environments, respectively (Fc = Fe(η -C₅H₄)₂).
13. Potentials are quoted relative to the ferrocene/ferricenium couple at E_{1/2} = 0.00. Polymer solutions were 1 x 10⁻³ M in CH₂Cl₂ with 0.1 M [Bu₄N][PF₆] as a supporting electrolyte. The working electrode was Pt and the reference electrode was a sce.
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Table 1. Thermal Copolymerization Experiments involving **1** and **3**

3 : 1 <u>mol : mol</u>	M _n (PDI)	M _n (PDI) ^a	λ _{max} (nm) (polysilane)	T _g (°C) ^b
2 0 : 1	250,000 (1.6)	230,000 (1.9)	-	33
5a 1 : 2.2	89,000 (3.5)	1,730 (1.4)	325	69
5b 1 : 1	75,000 (3.1)	1,410 (1.2)	330	-
5c 2 : 1	67,000 (2.4)	1,050 (1.4)	333	-
4 1 : 0	91,000 (3.0)	-	338	-

- a) M_n of the remaining oligoferrocenylsilane segments after irradiation with UV light (340 nm) in THF for 18 h.
- b) Determined by DSC.

Figure 1 ^{29}Si NMR Spectra of 5a and 5c in the Ferrocenylsilane Region

